

*Research Paper*

## **Determination of Heavy Metals in Forage Grasses (Carpet Grass (*Axonopus Ompressus*), Guinea Grass (*Panicum Maximum*) and Elephant Grass (*Pennisetum Purpureum*)) in the Vicinity of Itakpe Iron Ore Mine, Nigeria**

**Omono Christiana Matthews-Amune<sup>1,\*</sup> and Samuel Kakulu<sup>1</sup>**

<sup>1</sup>Department of Chemistry, University of Abuja, Abuja, Nigeria

\* Corresponding author, e-mail: (omonomatthews@ yahoo.com)

(Received: 14-10-12; Accepted: 16-11-12)

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**Abstract:** *The role of Livestock in the production of safe food has underlined its impacts on public health and food security. Samples of grasses Carpet Grass (*Axonopus lompressus*), Guinea Grass (*Panicum maximum*) and Elephant grass (*Pennisetum purpureum*) used as fodder grown on the vicinity of iron mine of Itakpe, Nigeria were analyzed for Cd, Cu, Mg, Ni, Pb and Zn. Samples from Ossara 12 kilometers away from Itakpe was used for comparison. All elements were determined by AAS. Mean concentration of total metal content of agricultural soils investigated gave  $0.16\pm 0.02$ ,  $0.15\pm 0.03$ ,  $0.04\pm 0.03$ ,  $0.1\pm 0.02$ ,  $0.07\pm 0.01$  and Zn  $0.04\pm 0.04$   $\mu\text{g/g}$  for Cd, Cu, Mg, Ni, Pb and Zn respectively. High levels of metals were found in the tailings (Mn 700, Pb 200, Cd 23, Ni 41, Fe 244,000  $\mu\text{g/g}$ ). Total concentrations of the elements in grasses were  $0.02\pm 0.01$ ,  $0.06\pm 0.01$ ,  $0.11\pm 0.02$ ,  $0.06\pm 0.04$ ,  $0.03\pm 0.01$ ,  $0.07\pm 0.01$   $\mu\text{g/g}$  for Cd, Cu, Mg, Ni, Pb and Zn respectively. Total concentrations of the elements examined were within ranges normally encountered in soils and the observed metallic levels of the grasses were below the FAO/WHO limit guideline values for heavy metal levels in food.*

**Keywords:** Heavy metals, Tailing, Mining, Livestock, Contamination.

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### **Introduction**

Although heavy metals are naturally present in soil, vegetation, and living organisms through the need for micro-elements, pollution comes, from activities such as mining, agriculture, vehicular air

pollutants, smelting and so on. (Hackinen, 1987, Onder et al., 2007, Gutiérrez-Ginés et al., 2010) Mining has been reported as a major source of heavy metal contamination to ecosystems with metals liberated in mine waste and tailings. (Gutiérrez- Ginés et al., 2010, Bruce et al., 2003) Mine minerals which are finely divided materials may find their way through the environment and food chain to organisms either by metal uptake in plants or direct ingestion of soil and tailing. (Bruce et al., 2003) According to Khan et al (2007) micro-nutrients present in the soil are transported to livestock through the forages on which they feed. Contamination by these heavy metals is a concern due to their potential for toxicity or long-term toxic effect on organisms through biological and pathological reactions resulting in health problems. (Onder et al., 2007, Gutiérrez- Ginés et al., 2010, Bruce et al., 2003) Thus it is important for uptake processes of heavy metals to be understood.

The role of livestock in the production of safe food is recognized worldwide, and events have underlined its impacts on public health and food security. (Gutiérrez- Ginés et al., 2010, Bruce et al., 2003, Ahmad et al., 2009) Concerns prompted by the outbreak of certain diseases have encouraged health professionals to scrutinize more closely their causes and methods for their control. (Bruce et al., 2003, Ahmad et al., 2009) Imbalanced nutrient availability, different physiological disorders and diseases have been traced to the presence of heavy metals in fodder plants. (Khan et al., 2007) These plants absorb essential minerals and heavy metals from the soil, through processes such as mining, soil fertilization practices and polluted air. This is of great concern for livestock due to their toxicosis effects. (Bruce et al., 2003, Pang et al., 2003, Boom, 2002).

Forage grasses such as Carpet Grass (*Axonopus lompressus*), Guinea Grass (*Panicum maximum*) and Elephant grasses (*Pennisetum purpureum*) are widespread and contribute significantly to feed for livestock in various countries. Fodder plants serve as source of essential metals for grazing animals and the mineral status of these forages is a function of multiple factors, which interact with one another to produce varied effects. (Kabaija and Smith, 1988) One of such factors is the differences caused by climatic changes. It is important to know the micro-nutrient concentrations of fodder plants because livestock performance is based largely on nutrition in terms of both quality and quantity. (Khan et al., 2007) *P.purpureum* is a robust perennial grass commonly found near river banks and is reported to have natural capacity to accumulate heavy metals. (Purwonugroho et al., 2007) *P.maxium* is a competitive weed that is widely distributed in the rainforest and savannah zone, succulent and palatable to animals especially cattle. *P.maxium* has been reported to have affinity for Cd and Au in soils. (Purwonugroho et al., 2007).

Various studies on the use of grasses as forage has been carried out in several countries where mining activities have been associated with varying levels of heavy metal contamination that has posed potential risks to inhabitants of surrounding settlements but none has been carried out in the Itakpe mine vicinity in Nigeria. The study is designed to determine the influence of mining activities on the levels of heavy metals in soil, tailings and some grass species (Carpet Grass (*Axonopus lompressus*), Guinea Grass (*Panicum maximum*) and Elephant grass (*Pennisetum purpureum*)) used as livestock feed.

## Materials and Method

The Itakpe mine site is located within longitude 6° 16'E and latitude 7° 36'N. The mining operation at Itakpe Iron Mine commenced in 1979 and Beneficiation in 1993. Mining and Beneficiation stopped in 2008. The climate of the area is tropical and consists of 6 months (May to October) of rainy season (RS) and 6 months (November-April) of dry season (DS). Samples were collected around the river Pompom stream that runs through the mining area where pastoral activity and particularly cattle grazing take place during the rainy and dry seasons. Samples for comparison were collected from Osara (7°41.821'N and 6°20.925'E). Grass species of interest, Carpet Grass (*Axonopus lompressus*), Guinea Grass (*Panicum maximum*) and Elephant grass (*Pennisetum purpureum*) (100 samples of each species the) were collected over 1 km stretch along the stream during RS and DS, as well as other randomly selected points to represent the grass that the cattle feed on (Fig. 1).The samples were

washed with deionized water, air dried and dried to constant weight at about 105 °C in an oven. Samples were ground into powder, passed through a 0.02 mm sieve, mixed to homogenize and stored in acid treated polythene bags. Method of 4:1 mixture of HNO<sub>3</sub> and HClO<sub>4</sub> by Kakulu and Jacob (2003) was used for plant digestion. Reagent blank was prepared in similar manner. Spiking of the sample was done using standards of concentration of each studied metal and extracted as above.

Surface soils (150 samples) were sampled with a stainless steel knife from the farm lands in the vicinity of the mine during the RS and DS. Soil samples were collected in nylon bags soaked in 10 % HNO<sub>3</sub> solution for 24 hours, rinsed with deionized water and air dried. Stainless steel knife previously soaked in 10 % HNO<sub>3</sub> solution for 24 hours and dried was used to collect soil samples to a depth of about 15 cm, and at about 50 m interval within each farmland. The collected samples were air-dried for seventy-two hours, ground in a mortar and passed through 0.005 mm sieve sieved to and stored in clean polythene bags. Tessier et al [12](1979) method for total metal analysis was carried out by digesting 1 g (<0.005 mm) of soil sample with a mixture of 5 ml HF and 1 ml HClO<sub>4</sub>. The extract was analyzed using AAS. Same procedure was carried out on soil Reference sample.

Tailings were sampled with a stainless steel knife from around the beneficiating plant. The collected tailings samples were air-dried for seventy-two hours and stored in clean acid treated polythene bags. Ukpebor and Unuigbe (2003) 3:1 mixture of HNO<sub>3</sub> and HClO<sub>4</sub> method was used for tailings digestion. The extract was analyzed using AAS.

Quality control was implemented through three replicate samples, reagent blank, spiking and use of international soil reference sample (Soil Reference Material 989 Netherland). Precision for the determination of heavy metal in grasses ranged 0.30-12 % and in soil ranged 8-12 %. Recovery studies gave 80-120 % for grasses. Analysis of soil Reference Material 989 from Netherland gave Cu 144.5±11.6 and Pb 253.8±13.8 µg/g against the standard values of 153±3.9 and 282±3.6 µg/g for Cu and Pb respectively.

## Results

Soil and grass samples were analyzed for heavy metals namely Cd, Cu, Mg, Ni, Pb and Zn and tailings for Mn, Pb, Cd and Ni. Table 1 shows the mean concentration of metals in grasses for the RS and DS, Table 2 summary of metallic concentrations in the tailings and Table 3 the summary of the concentration of metals in the soil samples for the RS and DS. All the studied elements were present in all the samples from both locations and occurred in varying amounts. There was no specific pattern in their variation during both seasons. The levels of all the heavy metals analyzed for were significantly higher in tailings than soil and grass samples. Results show metallic levels in soil to be significantly higher than the levels in grasses. Soil levels of heavy metals ranged from 7 times higher for Cd to 8 times higher for Cu except for Mg which was higher in grass than soil.

The metallic levels in grasses were low with significant differences in metallic concentrations observed between species. These variations reflect differences in nutrient uptake. There was no difference between the metallic levels in mining site grasses and control except for Zn and Ni in mining site which were higher than control during RS and Ni in mining site which was higher than control during the DS. In mining site relatively high metal level for Mg was observed during DS while relatively high level of Ni and Cu were observed during the RS. Cd metallic level was the same during RS and DS.

Tailings metallic level ranged 23 to 244,000 µg/g with Fe showing the highest level. The summary of the concentration of metals in the soil samples for the RS and DS are listed in Table 3. These sites show more than one heavy metal in the topsoil layers. The observed soil metal levels were generally low. There was no specific variation pattern between the RS and DS metal levels. Total soil concentration of Cd ranged 0.12-0.18, Cu ranged 0.08-0.18, Mg ranged 0.04-0.04, Ni 0.05-0.17, Pb ranged 0.05-0.07 and Zn ranged 0.04-0.04 µg/g. The total soil metal level for Mg was the same for

both seasons. Zn and Pb levels were relatively low (Zn 0.04-0.04 and Pb 0.05-0.07  $\mu\text{g/g}$ ). Total concentrations of the 6 elements examined were within ranges normally encountered in soils. (Pendias and Dubka, 1992, Bero and Reaves, 1984).

## Discussion

In mining environments dust laden metals spread as a layer of dust on every surface in the area due to blasting of the rocks during mining. These contaminants can be dispersed and transported downstream through atmospheric processes such as wind with the extent of metal removal from soil depending on factors such as mineralogy of tailings, total metal concentration, their speciation and the presence or absence of competing ions. (Onder et al., 2007, Gutiérrez-Ginés et al., 2010, Bruce et al., 2003) This indicates aerial deposition of metal particulates in the mining site. The elevated metallic levels in the samples could also be due to the addition of agrochemicals in agricultural soil and rain water washing (precipitation) on the plants. Metallic levels can be elevated when soil samples and grasses are taken near tailings deposits. According to Bruce et al (2003) elevated plant-adhered dust levels may be attributed to a higher splash effect from rain hitting the tailing material in the RS or dust dispersion in the DS. With the high level of Fe in the tailing there is a possibility of iron toxicity. For livestock, Fe is an essential component of haemoglobin and critical for a number of other body functions but cattle can consume large amounts of Fe in grazed pasture or by ingesting soil. Excessive Fe in pasture can interfere with Zn and Cu adsorption. Boom (2002).

The total metal concentration of the studied metals in Itakpe mining environment soil farm and the control farm were lower than that in the tailings. Generally, the levels of heavy metals were significantly higher for the Itakpe mining site soil than for the control site. Pollutants present in tailings and mine waste leads to metals scattering in the mine surroundings with continuous disperse by erosion, wind action and effluent draining them into arable land, rivers and ground waters and change in climate leading to seasonal variations in their metallic levels. (Onder et al., 2007, Kabaija and Smith, 1988, Bruce et al., 2003) The studied metals in soil had no specific patterns of distribution during both seasons. However there were variations in heavy metal levels in the soil during both seasons which could be due to changes in physicochemical properties of agricultural soils, non-equilibrium distribution of water and microbial mediated processes.

The variations observed during the RS could be due to flood which causes erosion and results in uneven distribution of metals in certain part of the soil, differences in the individual metal solubilities and dissolution of carbonates by acidic rain where the topography is sloppy. However anomalies in metallic levels could occur as a result of heavy metal deposition on soil surface from various sources such as emissions of metal-carrying dusts, gases and smoke from industrial undertakings through atmospheric transportation. (Gutiérrez-Ginés et al., 2010) These contaminated soils can influence the metal uptake by plants grown on the soil. High level of heavy metals in soil has been reported to cause morphological changes such as yellowing and browning, deformity in shape, spotting and drying of leaf margins. (Gutiérrez-Ginés et al., 2010, Ahmad et al., 2009).

The metallic levels observed in grasses could be as a result of the heavy metals absorbed from the soil and the dose received from plant-adhered dust with the more extensive areas of acid condition influencing the bioavailability of metals. (Khan et al., 2007) The metallic level observed on grasses showed that there was no specific pattern in the variation of metallic levels during both seasons. The observed difference in metallic levels between the soil and grasses indicates that only a fraction of the total metal content in the soil was taken up by the grasses. Heavy metals in plants are as a result of their absorption from the soil into roots and other plant parts with uptake varying with soil properties especially pH, plant species, type of metal and climatic conditions among others. (Khan et al., 2007, Boom, 2002).

The DS showed relatively high metal level for Mg. This agrees with previous report that the levels Mg were higher during the DS. (Kabaija and Smith, 1988) The higher Mg level observed during the

DS could be as a result of the use of moisture in photosynthesis since during the RS the water available is sufficient for the migration of essential metals to give enough nutrients to the grasses. According to Kabaija and Smith (1988) the level of Mg in grasses is dependent on the age of the grasses and their concentration increases during the DS. In plants, Mg is essential for the process of photosynthesis, with Mg being at the centre of the chlorophyll molecule. (Boom, 2002) Mg is essential for human, mammals and plants. Mg deficiency in cattle has been reported to cause effects such as nervous irritability, convulsions, scours and general ill-thrift, which can ultimately result in death. (Boom, 2002).

The RS showed relatively high level for Ni and Cu. This could be explained by the washing of Ni in the tailings and the possibility of use of agrochemicals for agricultural purposes in the vicinity. According to Kabaija and Smith (1988) fertilizer application causes increase in Cu concentrations. The observed high levels of Zn, Ni and Cu during the RS and low level during the DS agrees with Kabaija and Smith (1988) report but disagrees with Khan et al (2007) who reported no difference for Cu and Zn during both seasons. Cu is reported to interact strongly with trace minerals and macronutrients for absorption by the plants with Ca in the form of carbonate precipitating Cu, and making it unavailable for the plants. (Khan et al., 2007) When mineral nutrients in fodder plants are low for livestock requirements, changes in concentrations brought about by climatic, managerial or, seasonal influences can be significant factors in severity of deficiency states. (Kabaija and Smith, 1988) Cu is essential in many plant processes such as photosynthesis, protein and carbohydrate metabolism, and is also present in several enzymes. Cu deficiency in cattle can result in ill-thrift, weight loss, diarrhoea, rough hair coat or loss of hair, hair pigmentation and reproductive problems. (Boom, 2002).

Effects of heavy metals on grasses are influenced by environmental factors such as seasonal variations between seasons, species, transpiration rates, age of plant, temperature, radiation, water supply, soil fertility, leaf area, previous management level of reserve carbohydrates, organic constituents, tailings variability and degree and rate of defoliation by grazers. Furthermore the age of regrowth effects are reported to be modified by both season and fertilizer effects. (Khan et al., 2007, Onder et al., 2007, Valentine et al., 2010, Kabaija and Smith, 1988) Khan et al (2007) findings reported no significant variation in metallic status of forage due to seasonal changes. Some researchers have reported a reduction in metal levels with increasing plant maturity while others have reported older grass plants to have higher levels. Stress has also been reported to affect foliar elemental levels. (Onder et al., 2007).

Grasses generally have high silica content ranging from 1 to 13 %.[22] (Valentine et al., 2010) High level of silica has been reported to reduce intake of certain plants in animals and may reduce digestibility of fodder by forming insoluble compounds with trace elements such as Zn reducing their availability. (Valentine et al., 2010) This makes Zn deficient for both grasses and livestock. (Onder et al., 2007) Zn is an enzyme required for growth and reproduction in plants and animals. Zn deficiency in fodder affects protein levels while high Zn levels in the soil can suppress pasture productivity. (Boom, 2002).

There was no difference in mean Cd concentrations across sites. This suggests that Cd availability did not differ significantly between sites. The observation that Cd levels of soil were magnitudes higher than those of grasses was not surprising with the high Cd level in the tailings. This result points to potentially high risks of Cd toxicities in the area. Cd toxicity kills microorganisms present in soils responsible for nitrification, enzyme activity, biodegradation of organic contaminants and CO<sub>2</sub> production. In humans Cd toxicity accelerates osteomalacia and osteoporosis, skeletal damage and causes cancer. (Duruibe, 2007) The presence of Pb in the tailings could be as a result of the combustion of fossil fuel used in the equipment for mining process. The observed Pb, tailings levels of 200 µg/g could be dangerous for fodder plants. According to Adie and Osibanjo (2009) Soil Quality Guidelines for Agriculture in Canada requires that soils containing over 200 µg/g of Pb need not be used for agricultural purposes. Pb in the environment is mainly air borne and returns to soil, water, and plants as dust, and can become hazardous for grazing livestock. (Ahmad et al., 2009) Exposures to Pb poisoning are linked to reduced body immune system, reproductive diseases, damage

of CNS and kidneys, heart diseases, memory deterioration, osteoporosis and death at excessive levels. (Gutiérrez- Ginés et al.,2010, Duruibe, 2007, Adie and Osibanjo, 2009) Concentrations of Ni in grasses were higher than those in soil. This disagrees with Ahmad et al (2009) report that concentrations of Ni in grasses are generally lower than those in soils. Ni is reported to functions either as a co-factor or structural component in specific metallo-enzyme or as a bio-legend. Diets very low in Ni affects animal growth, development and reproduction. (Ahmad et al., 2009).

The observed metallic levels of the grasses were relatively lower than the FAO/WHO limit guideline values for heavy metal levels in food. Environmental levels of most metals are known to be affected by industrial, agricultural and environmental processes such as mining. Gutiérrez-Ginés et al., 2010, Bruce et al., 2003).

## Conclusion

Results of this studies show that mining activities around Itakpe mines have contributed to higher heavy metal presence in the environment. The soil and grasses samples had Cd, Cu, Mg, Ni, Pb and Zn within the FAO/WHO limit guideline values for heavy metal levels in food. The study showed presence of heavy metals in quantities that are within the tolerable limit for humans. However, long exposure to these metals might bring about bioaccumulation and become harmful to the health of the human. Some specific measures such as restricting the locations where animals are grazed to prevent and control hazards should be taken in order to safe-guard the livestock reared in this area from the toxic effects of these metals.

## Tables and Figures:

**Table 1:** Concentration ( $\mu\text{g/g}$ ) of heavy metals in grasses

Metal	Dry season		Rainy season		Mean Conc.
	Mining Site	Control	Mining Site	Control	
<b>Cd</b>	0.02±0.01 (0.01-0.03) <sup>a</sup>	0.02±0.01 (0.01-0.03) <sup>a</sup>	0.02±0.01 (0.01-0.03) <sup>a</sup>	0.02±0.01 (0.01-0.03) <sup>a</sup>	0.02±0.01 (0.01-0.03) <sup>a</sup>
<b>Cu</b>	0.02±0.001 (0.019-0.021) <sup>a</sup>	0.02±0.001 (0.019-0.021) <sup>a</sup>	0.10±0.01 (0.09-0.11) <sup>a</sup>	0.12±0.02 (0.10-0.14) <sup>a</sup>	0.06±0.006 (0.054-0.066) <sup>a</sup>
<b>Ni</b>	0.04±0.03 (0.01-0.07) <sup>a</sup>	0.01±0.01 (0-0.02) <sup>a</sup>	0.18±0.01 (0.17-0.19) <sup>a</sup>	0.10±0.01 (0.09-0.11) <sup>a</sup>	0.11±0.02 (0.09-0.13) <sup>a</sup>
<b>Mg</b>	0.09±0.01 (0.08-0.10) <sup>a</sup>	0.09±0.001 (0.089-0.091) <sup>a</sup>	0.02±0.003 (0.017±0.023) <sup>a</sup>	0.03±0.01 (0.02-0.04) <sup>a</sup>	0.06±0.04 (0.02-0.64) <sup>a</sup>
<b>Pb</b>	0.01±0.001 (0.009-0.011) <sup>a</sup>	0.01±0.002 (0.008-0.012) <sup>a</sup>	0.04±0.02 (0.02±0.06) <sup>a</sup>	0.04±0.02 (0.02±0.06) <sup>a</sup>	0.03±0.01 (0.02-0.04) <sup>a</sup>
<b>Zn</b>	0.03±0.003 (0.027-0.033) <sup>a</sup>	0.04±0.004 (0.036-0.044) <sup>a</sup>	0.11±0.005 (0.105-0.115) <sup>a</sup>	0.02±0.01 (0.01-0.03) <sup>a</sup>	0.07±0.01 (0.06-0.08) <sup>a</sup>

a=range

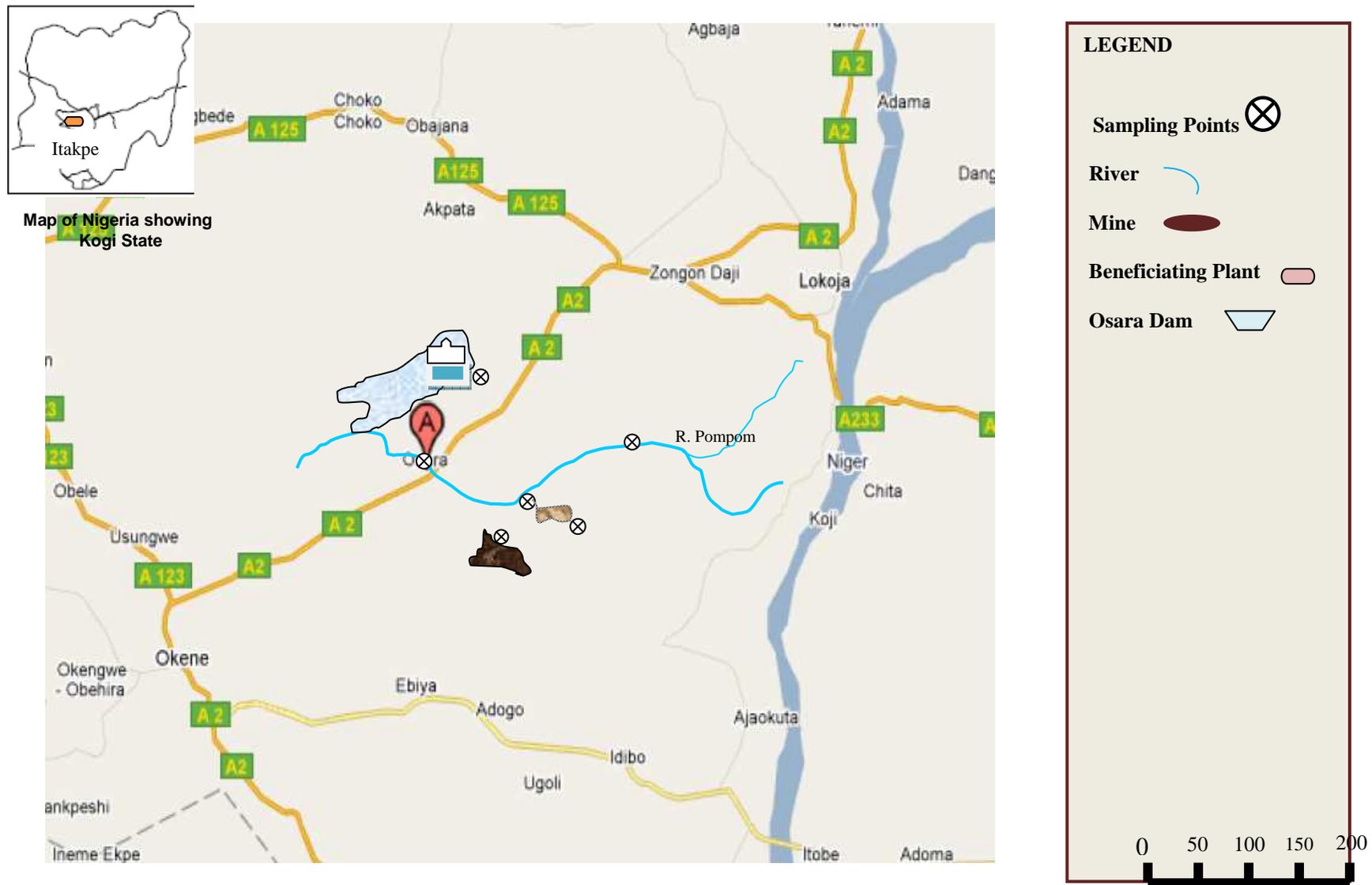
**Table 2:** Concentration ( $\mu\text{g/g}$ ) of heavy metals in the tailing

Metal	Concentration
Mn	700
Pb	200
Cd	23
Ni	41
Fe	244,000

**Table 3:** Summary of metal concentration ( $\mu\text{g/g}$ ) in soil

Metal	Dry season		Rainy season		Mean Conc.
	Mining Site	Control	Mining Site	Control	
<b>Cd</b>	$0.14 \pm 0.01$ (0.17-0.18) <sup>a</sup>	$0.07 \pm 0.01$ (0.06-0.08) <sup>a</sup>	$0.18 \pm 0.02$ (0.12-0.15) <sup>a</sup>	$0.10 \pm 0.01$ (0.09-0.11) <sup>a</sup>	$0.16 \pm 0.02$ (0.14-0.18) <sup>a</sup>
<b>Cu</b>	$0.16 \pm 0.03$ (0.08-0.18) <sup>a</sup>	$0.05 \pm 0.02$ (0.03-0.07) <sup>a</sup>	$0.13 \pm 0.03$ (0.14-0.17) <sup>a</sup>	$0.07 \pm 0.01$ (0.06-0.08) <sup>a</sup>	$0.15 \pm 0.03$ (0.12-0.18) <sup>a</sup>
<b>Mg</b>	$0.04 \pm 0.002$ (0.04-0.04) <sup>a</sup>	$0.04 \pm 0.002$ (0.038-0.042) <sup>a</sup>	$0.04 \pm 0.002$ (0.04-0.04) <sup>a</sup>	$0.03 \pm 0.003$ (0.027-0.033) <sup>a</sup>	$0.04 \pm 0.03$ (0.01-0.05) <sup>a</sup>
<b>Ni</b>	$0.07 \pm 0.01$ (0.05-0.09) <sup>a</sup>	$0.09 \pm 0.004$ (0.086-0.094) <sup>a</sup>	$0.15 \pm 0.03$ (0.13-0.17) <sup>a</sup>	$0.01 \pm 0.01$ (0.00-0.02) <sup>a</sup>	$0.1 \pm 0.02$ (0.08-0.12) <sup>a</sup>
<b>Pb</b>	$0.06 \pm 0.02$ (0.05-0.07) <sup>a</sup>	$0.06 \pm 0.001$ (0.059-0.061) <sup>a</sup>	$0.07 \pm 0.004$ (0.06-0.07) <sup>a</sup>	$0.02 \pm 0.001$ (0.017-0.021) <sup>a</sup>	$0.07 \pm 0.01$ (0.06-0.08) <sup>a</sup>
<b>Zn</b>	$0.04 \pm 0.05$ (0.04-0.04) <sup>a</sup>	$0.05 \pm 0.001$ (0.049-0.051) <sup>a</sup>	$0.04 \pm 0.03$ (0.03-0.04) <sup>a</sup>	$0.03 \pm 0.01$ (0.02-04) <sup>a</sup>	$0.04 \pm 0.04$ (0.00-0.08) <sup>a</sup>

a=range



**Figure 1. Map of Itakpe Mining Environment Showing Sampling Areas**

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